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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE 2935

THE GALVANIC CORROSION THEORY FOR ADHERENCE OF PORCELAIN-ENAMEL GROUND COATS TO STEEL

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SUMMARY

The galvanic corrosion theory of adherence between ground-coat porcelain enamels and steel was investigated as a part of a broad study of the bonding mechanism between ceramics and metals. The theory, which is outlined in detail in this report, is based on the mechanical anchoring of the enamel into the pits formed by the galvanic attack of the enamel on the steel surface. The theory was first examined from the standpoint of the data on adherence obtained in earlier studies at the National Bureau of Standards. In addition, several experiments were performed which demonstrated that galvanic corrosion of the metal base could occur during the short firing times encountered in enamel processing. On the other hand, certain inconsistencies were observed in the data which indicated that the mechanism of galvanic attack followed by mechanical anchoring was not the only important factor affecting the bond strength.

INTRODUCTION

Two investigations were recently completed at the National Bureau of Standards that have a definite bearing on theories heretofore advanced for explaining the adherence of vitreous base coats to steel. The first of these investigations, which involved the use of radioactive tracers, showed that cobalt from the enamel layer plates out on the steel during a normal firing operation (ref. 1). The second investigation, a report of which was prepared simultaneously with the present paper, showed that there is a positive correlation between the roughness of the coating-metal interface and the measured adherence (ref. 2).

The various explanations for the function of cobalt oxide in ground-coat enamels were reviewed in the light of these new findings.[1] One theory that appeared to be in agreement with the observed phenomena was

[1]A brief summary of the various theories to explain the function of cobalt in ground-coat enamels is given in reference 1.

the galvanic corrosion hypothesis. This was first postulated by Prof. Adolph Dietzel in 1935 (ref. 3). The theory had not gained wide acceptance as a valid explanation, possibly because Dietzel failed to establish that galvanic attack of the iron by the cobalt-bearing enamel did, in fact, occur during a normal firing operation. However, because of the apparent promise of galvanic corrosion in explaining the observed adherence phenomena with ground-coat enamels, a more detailed examination of the hypothesis was believed desirable. Numerous experiments were therefore performed in an attempt either to confirm or to disprove the theory.

The work described in the present paper constitutes a part of a broad study on the adherence of ceramics to metal which currently is being carried out at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

THE GALVANIC CORROSION THEORY

A schematic drawing has been found helpful in explaining the galvanic corrosion theory. Figure 1 is a drawing of this type. It shows a sequence of highly magnified interfaces between iron and two ground-coat enamels at three stages of a normal firing period. Figure 1(a) shows the change in interface with firing time for a cobalt-free ground coat while figure 1(b) illustrates the change in interface when a small amount of cobalt oxide is present. It is assumed for this schematic drawing that the iron was polished flat before the enamels were applied.

First consider the enamel with no cobalt. The diagram on the left in figure 1(a) represents the condition of the interface shortly after the coating has dissolved the oxide layer, that is, quite early in the firing cycle. There of course will be some oxidation of the iron before the enamel fuses, but in the schematic drawing the interface is considered at the stage just following the time when the oxide layer is first dissolved. The second diagram in figure 1(a) represents the condition of the interface a minute or two later; and the third picture (fig. 1(a)) represents the interface after a normal firing of 4 to 6 minutes. The distance to the interface from the reference line, drawn in the figure as an extension of the interface line in the first sketch, represents the depth of corrosion at any location. The drawing, which was made after numerous observations of sections under the metallographic microscope, shows that the iron is being corroded, but that it is being corroded uniformly. The interface is still smooth after a normal firing and because of this smoothness there can be no mechanical anchoring of the coating to the metal. Some adherence will develop with a smooth

interface of this type, but according to the theory it will be a weak type of adherence. In fact, unless special steels are used, such as a titanium-bearing, low-carbon steel, an enamel that contains no adherence oxides will flake from the metal on cooling, because of excessive hydrogen pressure at the interface (ref. 4).

The corrosion of the iron when cobalt ions are present in the enamel layer is of a different type. When an enamel fuses, it first wets the oxide layer that is formed on the iron during the heatup, that is, while the initially cold specimen is approaching furnace temperature. As soon as the oxide layer is dissolved, cobalt from the ground coat begins to plate out in the cathodic areas of the iron surface. This is shown schematically in the first diagram in figure 1(b).

That metallic cobalt does in fact deposit on the iron during a normal firing was demonstrated by the radioactive tracer work (ref. 1) and by the recent X-ray spectrographic study of Patrick and coworkers (ref. 5). That the cobalt would plate out first on cathodic areas of the iron surface is in keeping with the galvanic corrosion theory. Mears and Brown (ref. 6) list as many as 10 different factors that will produce potential differences on a metal surface immersed in an electrolyte. The molten ground-coat enamel is an electrolyte having a conductivity at the firing temperature estimated to be of the same order of magnitude as that of a molten glass high in alkali or about 0.20 mho (ref. 7). It is logical to believe that potential differences could exist on an iron surface covered with enamel from such factors as the grain boundaries being anodic with respect to grain interiors, or one metal grain at the surface being anodic with respect to an adjacent grain with a different orientation. Assuming that such potential differences do exist, cobalt will plate out first on the cathodic areas. The plating reaction might be written $Fe + Co^{++} \rightarrow Fe^{++} + Co$. One such area is shown schematically in the first diagram in figure 1(b). The instant the cobalt makes electrical contact with the iron a tiny galvanic cell is formed in which the iron acts as the anode and the cobalt-plated area as the cathode.

The second diagram in figure 1(b) is schematic of the same cell a minute or two later. In this picture, iron is going into the molten enamel as Fe^{++} ions. Electrons are given up in the process. These flow to the cobalt-plated area where they create a reducing condition. Any aerial oxygen dissolved in the glass could pick up these electrons and become O^{--} ions, and any easily reduced metallic oxides, or for that matter even dissolved water in the glass, would tend to be reduced. For the galvanic cell to function, there would need to be the same number of O^{--} ions formed at the cathode as there are Fe^{++} ions at the anode.

Therefore, if the supply of oxygen at the cathode should be shut off for any reason the flow of electrons could not continue and the corrosion process would come to a stop.

The galvanic cell action would, of course, produce a preferential attack on the iron surface. This is shown schematically in the second diagram in figure 1(b). It is easy to visualize that the cathodic areas as illustrated in this diagram would provide anchor points to key the coating to the metal. Corrosion would be proceeding rapidly, however, and the stage shown in this diagram would change with firing time to the stage shown in the third diagram of figure 1(b), in which continued corrosion has caused a fragment of the steel to become detached.[2]

Figure 2 is a highly magnified interface between a cobalt enamel and a polished iron surface. The specimen from which the section was cut was fired for 4 minutes at 1,575° F. It is not difficult to conceive that several of the metallic particles near the interface in this photomicrograph were still attached to the underlying metal only shortly before the firing was terminated, just as the segment of metal illustrated in the second diagram of figure 1(b) is shown as becoming detached in the third diagram of figure 1(b). However, cobalt ions are still present in the coating at the stage shown in the third diagram (fig. 1(b)). Hence, while some anchor points have lost their effectiveness, new galvanic cells and consequently new anchor points can form. The interface can, in fact, be looked upon as being in a constant state of flux, but it is one of the requirements of the galvanic theory that as long as a large number of these anchor points are at the interface[3] the coating will show the strong adherence that is typical of cobalt-bearing enamels.

The galvanic theory as outlined above, while containing many of the authors' own conceptions of the mechanism, is still in substantial agreement with the hypothesis originally presented by Dietzel (ref. 3). The picture given by Dietzel was as follows: The precipitated nickel (or cobalt) in contact with the iron base forms a couple, or short-circuited

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[2]The schematic drawing, like a metallographic section, is a two-dimensional representation of a three-dimensional phenomenon. Therefore, although the metallic globule illustrated in the third diagram of figure 1(b) appears to be detached from the base metal, it may actually be joined either above or below the plane of sectioning. Careful study of actual sections after etching with hydrofluoric acid indicates that many of these globules that appear near the interface are, in fact, still joined to the metal.

[3]Reference 2 shows a cobalt enamel to have approximately 600 anchor points per centimeter after a normal firing. Squaring this value gives 360,000 anchor points per square centimeter or 37,152,000 anchor points on one face of a 4- by 4-inch specimen.

local cell, in which iron is the anode and nickel, the cathode. The current (positive electricity) flows from the iron through the melt (molten coating material) to the nickel and back to the iron. During firing, these couples are not exhausted, because there is an abundance of iron on the anode side and diffusing atmospheric oxygen has a depolarizing action on the cathode side. The result is that the iron goes continuously into solution, the surface becomes roughened, and the enamel anchors itself into the holes.

Staley (ref. 8) was one of the first to believe that cobalt plated out on the iron during a normal firing of an enamel ground coat. At the same time, Staley did not associate the plating-out action with galvanic attack on the iron surface but, on the contrary, believed that the cobalt plating retarded oxidation of the iron and thus preserved the rough grippable surface imposed by acid pickling.

EXPERIMENTAL PROCEDURES AND RESULTS

Corrosion of anode in coated metal-to-metal couples.- In investigating the validity of the previously described theory, it was desirable to learn whether galvanic corrosion could occur under the conditions encountered during the short firing periods used in applying an enamel to steel. To obtain such information, several experiments were performed.

The first of these experiments was made by electroplating cobalt on the lower half of an iron specimen and, after application of a porcelain enamel free of adherence oxides, sectioning the specimen to determine whether there was any increase in corrosion of the iron surface at the point where it met the cobalt plate. This method gave inconsistent results. Good adherence of the electroplated cobalt to the iron was not achieved in all cases nor was the demarcation between the edge of the plated cobalt and the iron always clearly defined.

To overcome these deficiencies a new technique was devised in which plugs of iron 3/16 inch in diameter were "cold-forged" into holes punched out of 3/4- by 2- by 0.050-inch sheets of cobalt, nickel, and copper, respectively. In addition, beryllium and copper plugs were cold-forged into specimens of iron. The cold-forging operation was performed by vigorously hammering the plugs into the specimen on a flat anvil surface. After forging, one surface of the specimen was ground and polished. A ground coat, free of adherence oxides, was then applied to the polished face only and the specimen subjected to a normal firing. After cooling, the specimen was examined visually after which it was sectioned through the plug.

The visual observations yielded valuable information. The enamel used for the experiments was free of coloring oxides. When fired in air on a metal base such as copper, iron, or cobalt, the coating picked up metal ions that colored the glass and the change in color intensity could be taken as a qualitative measure of the amount of oxidation or corrosion of the metal base. Figure 3 shows the changes in shading in the case of the copper-iron specimens. In figure 3(a) the dark band at the periphery of the iron insert indicates a greater corrosion over this area. The "halo" over the copper surrounding the insert is believed to indicate cathodic protection of the copper by the iron. It was much lighter in color than the remainder of the copper sheet, where there was not sufficient cathodic protection to prevent the introduction of copper ions into the coating. The diminution in number of bubbles in the enamel at the halo is a phenomenon for which the authors have found no satisfactory explanation. In figure 3(b), the area of the anode (iron) was large while that of the cathode (copper) was small. Much less corrosion of the iron occurred under these conditions which indicates that the system was under cathodic control (ref. 9).

When the aforementioned specimens were sectioned and the junctions examined under the microscope, the visual observation was confirmed. On the iron insert in the cobalt specimen the corrosion of the iron was found to be concentrated near the junction, as shown in figure 4,[4] but for the iron insert in copper the corrosion extended back some distance from the junction. Another observation of interest was the presence of an oxide layer on the iron near the junction of the iron-in-copper specimen indicating that the iron oxide was forming faster than the glass was capable of dissolving it.

In most cases no appreciable slippage of the plug in the specimen hole occurred during the firing operation, although what might be considered as true welding (in which diffusion during firing probably played a part) was noted only in the case of the iron-cobalt junctions.

Depth of corrosion of iron during firing.- Galvanic corrosion usually produces an accelerated attack on the anodic member of the cell. To determine whether such is the case when a cobalt-bearing ground coat is applied to an iron base, the following tests were made: A small (0.053-inch diameter) hole was drilled in each of a series of ingot-iron

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[4]Sections through the cobalt-plated specimens that had been enameled also showed more corrosion of the iron adjacent to the iron-cobalt junction, thus ruling out the possibility that local cold-work of the metal during the cold-forging operation could have been responsible for the observed effects.

specimens, and a wire of gold dental alloy 0.052 inch in diameter was inserted into each hole.[5] The wire was cut off almost flush with the iron surface, and the wire then brazed into the hole with an oxygas torch, borax being used as a flux. The surface of each specimen was next ground flat and polished after which four of the specimens were coated with a typical ground-coat enamel containing 0.8 percent cobalt oxide (Co_3O_4) and another four coated with the same enamel except that it contained no cobalt oxide. The firing times at 1,575° F were 2, 4, 8, and 16 minutes.

Figure 5 shows a photomicrograph of a section taken from the specimen with the cobalt-free enamel which was subjected to the 2 minutes' firing time. The gold alloy serves as a reference line indicating the original level of the iron surface. The increased attack near the junction, which is undoubtedly caused by galvanic action, is not pertinent to this particular experiment. The important observation in figure 5 is the distance d. This was taken as a measure of the depth to which the iron corroded during firing. In the case of the specimens coated with cobalt-bearing enamels, the interface was not smooth and d was measured to the bottom of the pits in the iron surface. It was assumed in all of the measurements of this type that the gold alloy did not oxidize and therefore that its surface maintained the same level throughout the various firings.

Figure 6 shows the depth of corrosion plotted against firing time for both the cobalt-bearing and cobalt-free enamels. It is evident from these curves that cobalt does in fact accelerate the corrosion of the iron just as the galvanic theory would imply. However, because the corrosion was nonuniform when cobalt was present in the enamel, the differences in the amount of iron oxidized are not so great as might be inferred from the curves. As mentioned previously, the distance d for the cobalt-bearing enamels was measured to the bottom of the pits. The normal corrosion, that is, disregarding selective attack, seemed to be the same for both enamels. The increased corrosion with the cobalt-bearing enamels is represented, therefore, by the amount of material removed from the pits formed by the selective attack.

A second series of tests was made to determine both the effect of cobalt content and the effect of other adherence oxides on the depth of corrosion of the iron during a normal firing. Figure 7 is a plot of these data. It will be noted from this figure that increase in the cobalt-oxide content increased the depth of corrosion of the iron.

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[5]The gold alloy was used for the insert rather than gold because the alloy (a precipitation-hardening type) was sufficiently hard to prevent flowing of the metal during the polishing operation.

Nickel oxide when added as 0.8 percent by weight increased the corrosion depth over what was obtained when no adherence oxides were present. Arsenic trioxide behaved similarly. Copper oxide and antimony oxide, on the other hand, gave no increase in corrosion depth.

Analogous corrosion of iron in aqueous solutions.- The electrical conductivity of a ground-coat enamel at the firing temperature is estimated to be of the same order of magnitude as that of a 3-percent-by-weight solution of sodium chloride at room temperature. In both cases the conduction is ionic and both electrolytes are corrosive to steel under oxidizing conditions, that is, if dissolved oxygen is present. The type of attack on iron in an aerated 3-percent sodium-chloride solution might, therefore, be considered analogous to the attack by a molten enamel electrolyte during firing in an air atmosphere. For the same reasons, ions more noble than iron when present in either electrolyte should have roughly comparable effects on the type of attack and on the rate of corrosion of the iron. For this to be true, the order of the electrode potentials in the molten electrolyte should be the same as the order in an aqueous sodium-chloride solution. The potentials in molten enamel have not been determined, but no important reversals in order are believed to occur.

With this analogy in mind, experiments were performed with aqueous solutions of sodium chloride. In the first test, ingot-iron specimens with polished surfaces were immersed in about 400 milliliters of 3 percent sodium chloride for 4 hours at room temperature. Air was allowed to bubble through the solution at a constant rate of about 5 cubic centimeters per minute. Examination of the specimens after test showed a minor amount of corrosion with practically no selective attack. The test was then repeated with similar specimens except in this case 0.2 percent of cupric chloride was added to the freshly prepared solution of 3 percent sodium chloride. After 4 hours at room temperature the specimens were removed and examined. Considerably more corrosion of the iron had occurred than when the cupric chloride was absent. In addition, the surface was deeply pitted, indicating a selective type of attack. When cobaltous chloride was used rather than cupric chloride, the same effects were noted but to a lesser degree.[6]

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[6]It has been known for many years that iron may be corroded and pitted by an aqueous electrolyte that contains salts of a metal more noble than iron. However, no data could be found in the literature in which the salt concentrations were low and the electrolyte was an aerated sodium-chloride solution; hence, the described experiments were performed.

DISCUSSION

As mentioned in the introduction, the principal purpose of the present paper is to examine critically the galvanic corrosion theory of adherence. The experimental work described in the preceding sections is positive in showing that galvanic corrosion can occur in the enamel-iron system just as it occurs on iron that is immersed in an aqueous electrolyte. Further, the data show that appreciable galvanic corrosion can occur in iron-cobalt couples during the short firing times encountered in normal enameling operations. The companion paper (ref. 2) shows good correlation between anchor points on the iron surface and adherence index so that, from first inspection, it would appear that the Dietzel theory of galvanic attack on the iron by the molten enamel electrolyte, followed by mechanical anchoring of the enamel into the resulting pits, is an excellent explanation for the function of adherence oxides in ground-coat enamels. When the data from both papers are scrutinized, however, several anomalies appear that are in need of explanation before the theory can be fully accepted. A discussion of these anomalies follows.

(1) Why does copper oxide fail to perform as an adherence oxide? The present study shows that a copper-iron couple in an electrolyte of molten enamel produces galvanic corrosion of the iron as an anode. From these results, it is logical to expect from the theory that copper oxide in the ground coat would act as a good adherence oxide. That such is not the case is shown by the data of the companion paper (ref. 2). The data in this paper showed that copper oxide not only failed to aid the adherence by any measurable amount when added as 0.8 percent by weight[7] but also failed to increase appreciably the surface roughness except in the case of the sandblasted specimens. Figure 7 also shows no increase in corrosion depth when copper oxide was present in the ground coat.

This failure of the copper-bearing enamel to promote adherence on iron has been discussed by Dietzel (ref. 10). Dietzel found that copper oxide was reduced to metallic copper when iron oxide was present in the enamel. Iron-oxide contents as low as 1 percent were capable of causing the reduction of copper oxide while 10 percent iron oxide was necessary before nickel oxide was reduced. Thus, he concluded that copper is reduced by the iron-oxide-rich enamel layer near the interface before it can make contact with the iron surface. Because the metallic copper never reaches the iron, no galvanic cells can be formed and no pitting of the iron surface occurs.

Unfortunately such a hypothesis fails to explain why the enamel containing copper oxide did not give good adherence on a sandblasted

[7]The same coating with lower contents of copper oxide (down to 0.01 percent by weight) also failed to improved the adherence.

surface. In the companion paper, an anchor point count of 693 per centimeter was obtained for the copper-bearing enamel on sandblasted iron as against 173 per centimeter for the same enamel with no copper oxide. This count of 693 should be sufficient to produce good adherence if these specimens followed the general pattern, but the measured adherence index was only 7.0. No satisfactory explanation for this behavior has as yet been devised.

(2) Why does the roughening produced by sandblasting fail to produce the same powerful adherence as the roughening that is produced by the enamel during firing? The data in reference 2 show that roughening of the iron surface caused by sandblasting prior to application of the coating had only a minor effect on adherence as compared with the roughening caused by the attack of the molten ground coat. The explanation for this behavior as given by Dietzel (ref. 10) is that when the roughness is caused by galvanic corrosion the enamel is already in contact with the metal surface and thus penetrates readily into the pits and crevices as they are formed. When roughness is imposed prior to fusion, however, the small cavities are pocketed by entrapped air, thus preventing the access of the molten enamel.

The present authors find it difficult to accept such an explanation. It was observed in the work described in reference 2 that the enamel penetrated readily into the pits and crevices caused by sandblasting. Therefore, if it is accepted that good penetration of the roughened metal surface is always achieved, as the authors' observations would tend to indicate, then it follows that comparable adherence should be obtained whether the anchor points were formed by galvanic attack or by sandblasting.

It was observed in the present study that the anchor points on the iron surface formed from sandblasting tended to be larger than and of a somewhat different type from those produced by the galvanic attack of the molten enamel. However, if the bonding is caused by mechanical anchoring, it would seem that the strength of the bond should be mainly dependent on the number of anchor points per unit of area. It appears, therefore, that if adherence is caused solely by mechanical gripping then comparable adherence should be obtained whether the anchor points were formed by galvanic attack or by sandblasting prior to enameling. The observation that such is not the case indicates that mechanical gripping is not the only factor responsible for adherence development.

(3) Why does antimony oxide in the ground coat produce surface roughening (and fair adherence) on an iron surface that has been pickled and yet have no appreciable effect on a polished or a sandblasted surface? No explanation for the anomalous behavior of antimony could be devised by the authors that would conform with the galvanic corrosion theory.

These apparent contradictions are weaknesses of the theory. On the other hand, there are several perplexing questions about adherence that are readily explained by galvanic corrosion. For example, the galvanic corrosion theory explains why oxygen is necessary during firing. Further, it explains why the iron surface becomes pitted during firing when adherence oxides are present in the enamel. In fact, it might even explain the adherence-promoting function of the nickel dip.[8] The nickel, according to this explanation, would be expected to plate out preferentially on cathodic areas of the iron surface during the treatment in the nickel-sulfate solution. If an enamel were later applied to such a surface, active galvanic cells with nickel cathodes and iron anodes would be produced as soon as the enamel melted and became an electrolyte. The adherence with nickel-dipped steel would, under the suggested mechanism, be caused by galvanic corrosion followed by a mechanical anchoring of the enamel to the roughened steel surface. Such an explanation of the function of the nickel dip, however, should not be accepted without confirming experimental evidence. The investigation of the nickel dip was outside the scope of the present paper.

The observed small increase in corrosion of the iron when cobalt is present in the ground coat is explainable by galvanic corrosion. This increase in corrosion had been noted previously by Kautz (ref. 11) who postulated that the cobalt in the enamel acted as an oxygen carrier; that is, that cobalt, by changing its valence state, passed oxygen through the enamel layer to the iron surface. According to Kautz, this mechanism preserved an oxide layer at the interface and this oxide layer, in turn, was responsible for the adherence. The present work does not prove that such a mechanism could not be active, but it is believed that the galvanic theory does present a more likely explanation for the observed increase in corrosion of the iron surface.

CONCLUDING REMARKS

A critical examination of the galvanic corrosion theory of adherence indicates that the theory has some merits in explaining the function of cobalt in ground-coat enamels. It was demonstrated that galvanic corrosion can occur in a molten enamel electrolyte under normal firing

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[8]The nickel dip, or nickel pickle, is widely used in enamel operations to improve the adherence of the ground coat to the steel. It consists of pretreating the previously cleaned steel sheet in a dilute solution of nickel sulfate prior to coating application. The pH of the solution of this treatment is adjusted to obtain optimum galvanic deposition of nickel.

conditions. Further, it was shown in the companion paper (NACA TN 2934) that there is a good correlation between adherence and the number of anchor points on the iron surface. Thus, there is good supporting evidence that the powerful adherence developed with cobalt enamels is caused by mechanical anchoring of the coating to undercuts formed on the iron surface by galvanic corrosion resulting from cobalt-iron couples. However, the theory is weakened by (1) its failure to explain adequately why copper oxide does not perform as an adherence oxide and (2) why undercuts produced by sandblasting do not result in the same powerful adherence as the undercuts produced by galvanic corrosion. It is even possible, but not probable, that the good correlation between surface roughness and adherence as reported in the companion paper is fortuitous and that the anchor points are related to some second effect which in turn is the true cause of the bonding mechanism. It is felt, however, that this secondary effect, if such exists, must in some way be connected with the corrosion of the iron that occurs when adherence oxides are present.

National Bureau of Standards,
Washington, D. C., October 1, 1952.

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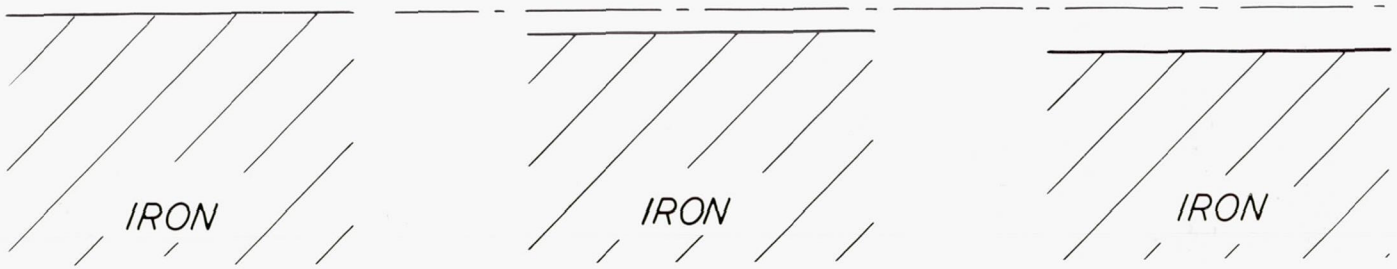
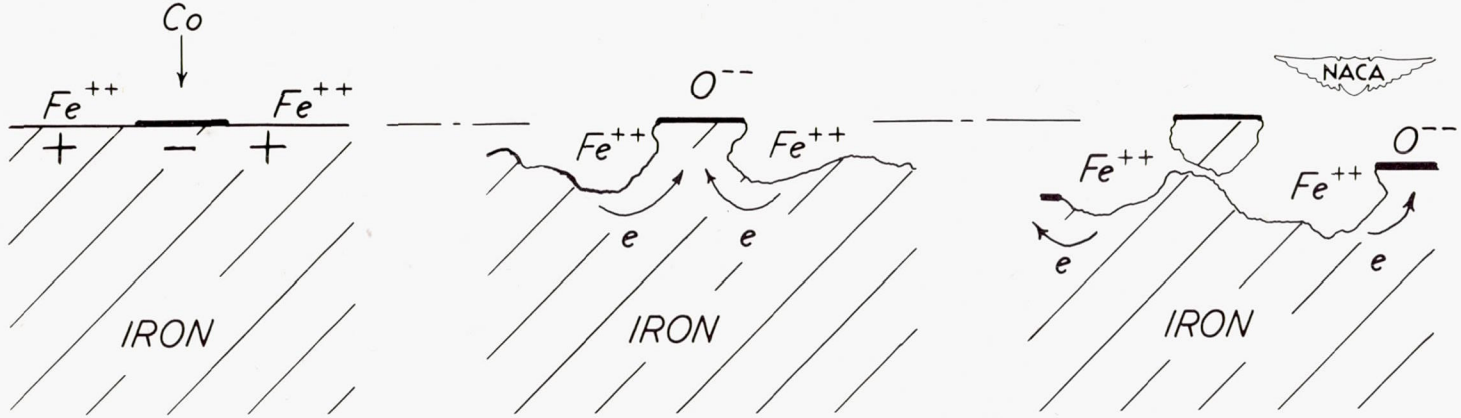


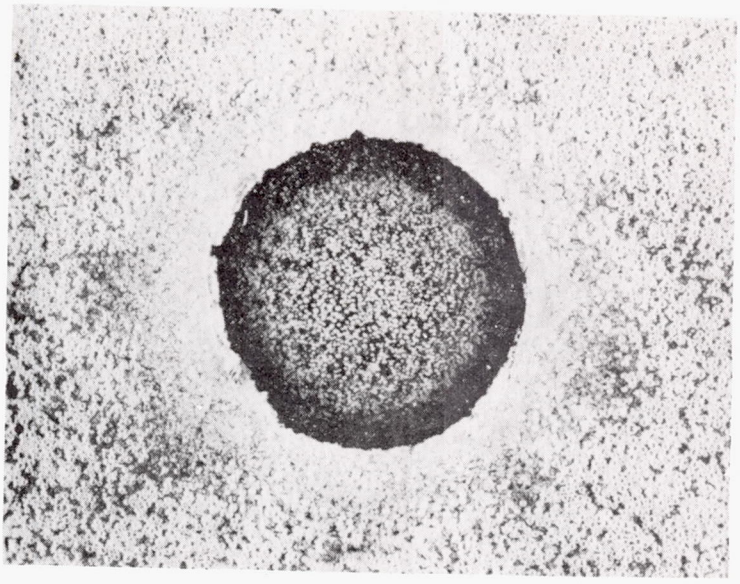
(a) No cobalt.



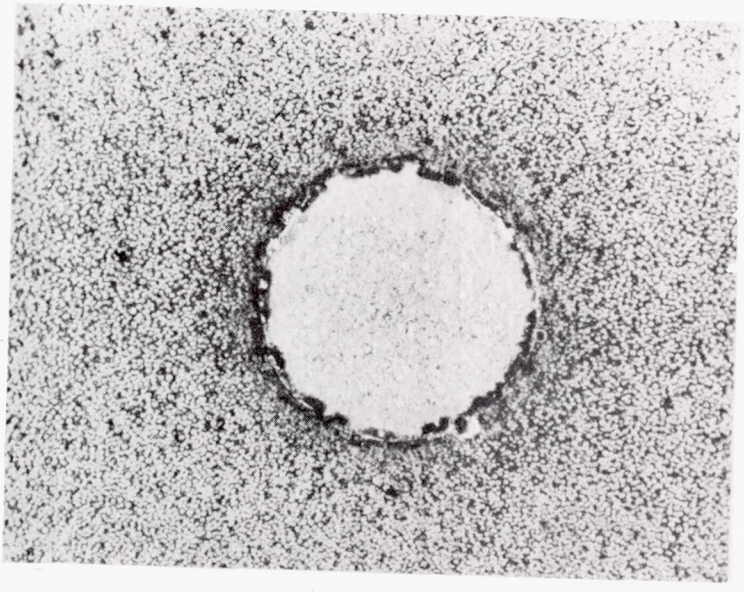
(b) Cobalt bearing.

Figure 1.- Schematic drawing illustrating the differences in corrosive attack on iron by cobalt-free and cobalt-bearing ground coats. Firing time increases in both sets of diagrams from left to right, the first diagram in each case indicating interface condition shortly after enamel fuses.

Figure 2.- Interface between ingot iron and a normally fired ground-coat enamel containing 0.8 percent by weight Co_3O_4. Iron surface was polished prior to coating. Unetched; X2,000.



(a) Copper specimen with iron plug.



(b) Iron specimen with copper plug.

Figure 3.- Photomicrographs taken normal to surface of a clear ground coat applied over composite specimens of iron and copper that were flat ground prior to coating. Darker areas indicate regions of accelerated corrosion of iron anode. Firing in both cases was 4 minutes at 1,575° F. Oblique illumination; X10.

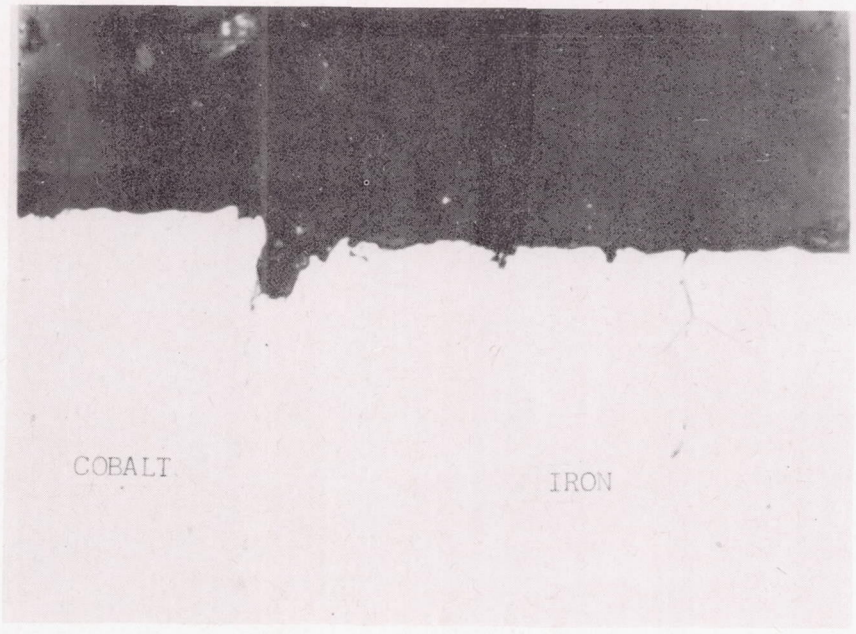


Figure 4.- Section through a coated specimen consisting of an ingot-iron plug cold-forged into a sheet of 18-gage cobalt metal. Surface of composite specimen was ground and polished prior to application of cobalt-free ground coat. Note greater corrosion of iron near the junction. Nital etch; X1,000.

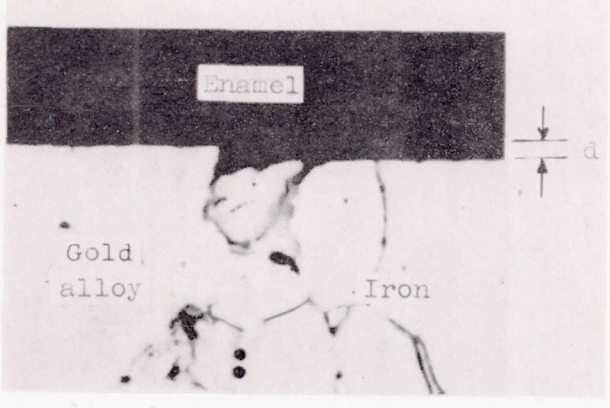


Figure 5.- Illustration of technique for measuring depth of corrosion of iron (distance d) that occurs during firing. Specimen used for illustration was coated with a cobalt-free enamel. Firing was 2 minutes at 1,575° F. Nital etch; X1,000.

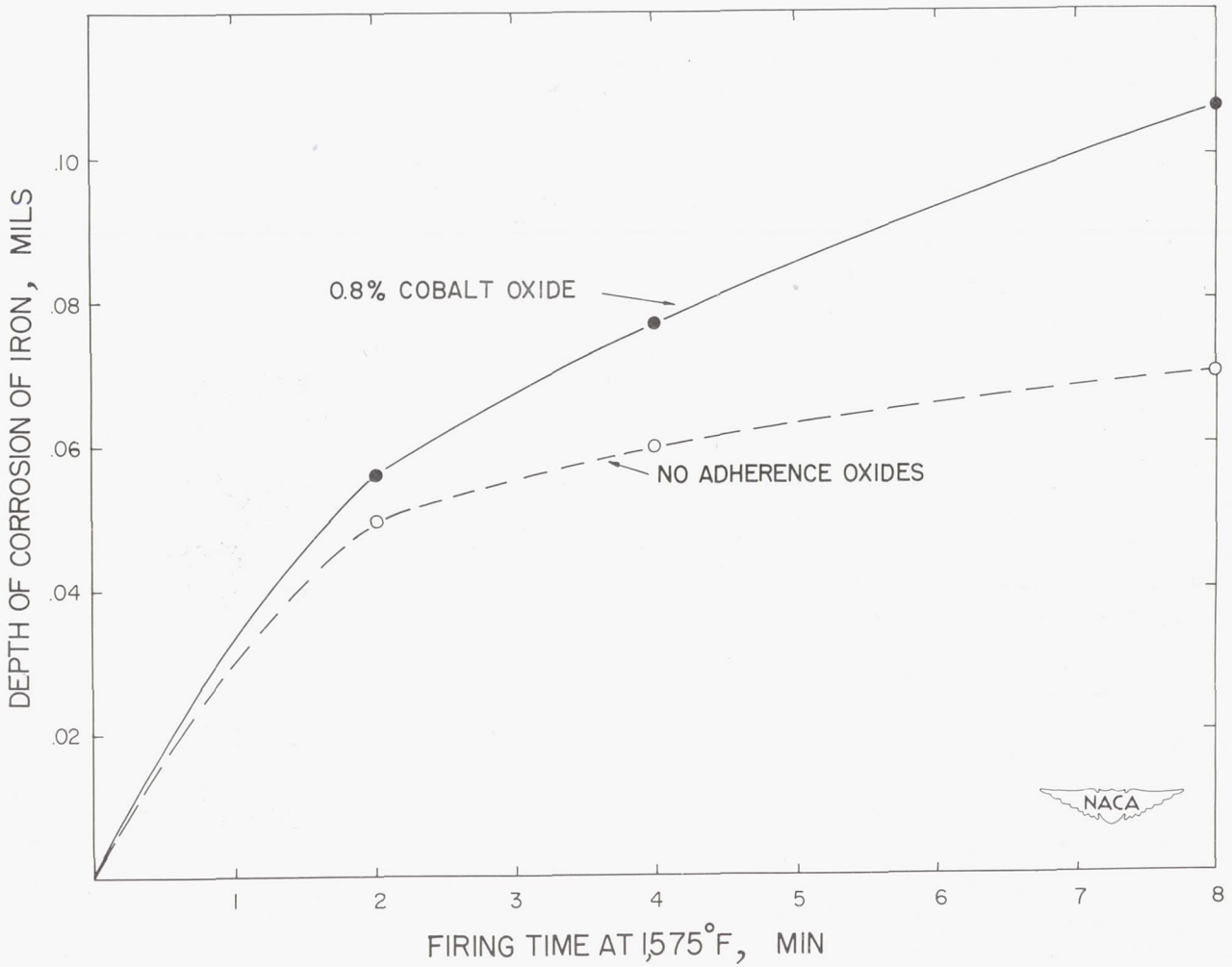


Figure 6.- Depth of corrosion of iron (d in fig. 5) plotted against firing time for two ground-coat enamels that were alike except for cobalt-oxide content.

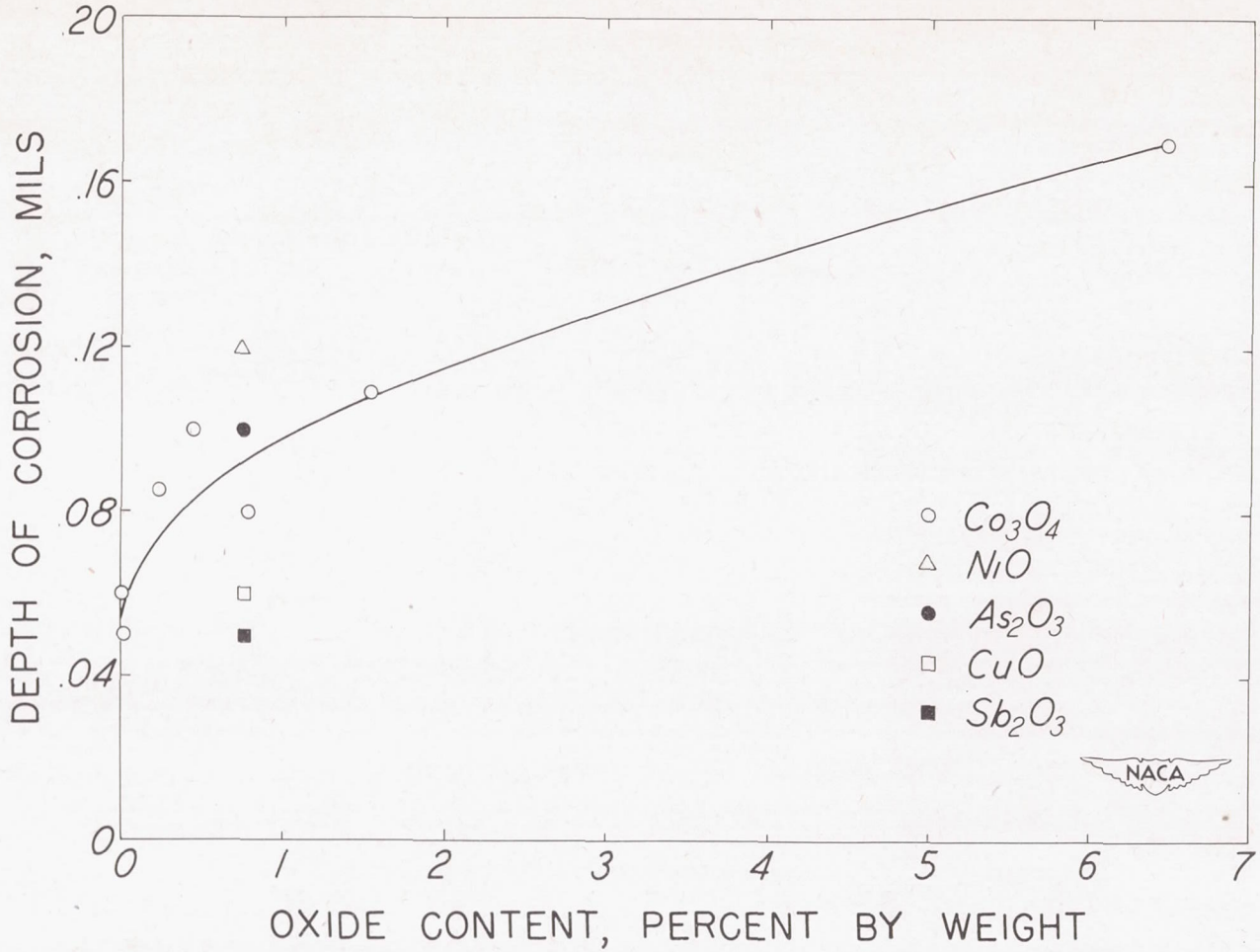


Figure 7.- Depth of corrosion (d in fig. 5) for specimens of ingot iron coated with ground coats that were the same except for varying cobalt-oxide content. Data for four other oxides when added as 0.8 percent by weight to same base ground coat are included for comparison. All specimens were fired 4 minutes at 1,575° F.

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